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Technical Progress in the Development of Zero Emission Coal Technologies

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Abstract

We present an update on the development of technologies required for the Zero Emission Carbon (ZEC) concept being pursued by ZECA Corporation. The concept has a highly integrated design involving hydrogasification, a calcium oxide driven reforming step that includes simultaneous CO_2 separation, coal compatible fuel cells for electricity production and heat recovery, and a closed loop gas system in which coal contaminants are removed either as liquids or solids. The process does not involve any combustion and as such has neither smokestack nor air emissions. An independent assessment of the concept by Nexant, a Bechtel affiliated company, suggests a net efficiency of approximately 70% for conversion of the higher heat value fuel energy into electrical output. This is even after the penalties of carbon dioxide separation and pressurization to 1000 psi are taken into account. For carbon dioxide sequestration a variety of options are being considered, which include enhanced oil recovery in the near-term and mineral carbonation as a long-term approach. We report on our early results in the development of sulfur tolerant anode materials for solid oxide fuel cells; a critical analysis of the calcium oxide – calcium carbonate cycle; trace element removal; and the recent results of hydrogasification tests.

History

The Zero Emission Coal Alliance (ZECA) was formed in the year 2000. As of March 2001, the Alliance included 18 members from private industry and government agencies. The Alliance was about evenly divided between Canadian and United States members. The private sector members were from the coal and minerals mining industries, and electric power generation and associated industries. The interests of the Canadian oil sands industry were strongly represented in the Alliance by the Alberta Energy Research Institute (AERI). In November of 2002, certain members of ZECA formed ZECA Corporation[1] to continue the pursuit of the technologies discussed below.

ZECA Corporation was formed to pursue 'Zero Emission' coal and carbon technologies and chose to focus on the ZEC concept originated at the Los Alamos National Laboratory (LANL), and that had, in part, been advanced by an existing U. S. Department of Energy program for mineral carbonate CO_2 sequestration[2], with work performed at Los Alamos, the Albany Research Center, the National Energy Technology Laboratory, and the University of Arizona. The overall concept includes a unique fossil feedstock gasification system to produce hydrogen and electric power, and a stream of CO_2 suitable for carbonate sequestration or alternative processes to dispose of CO_2. This paper discusses the ongoing work in the areas of coal gasification to power production.

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Introduction

The more developed countries such as the US and Europe have both a per capita energy consumption and economic wealth (GDP) that is 5 times the global average. Simply bringing the existing world's population to the same average standard of living as that now enjoyed by developed nations would imply the need for 5 times as much energy consumption. Considering that the world's population is likely to double during this century, it may take 10 times as much energy to satisfy the world's demand. If these numbers appear improbable, it must be remembered that this is the same rate of increase (2.3% per year) that took place in the last century. Developing nations will not be denied their share of energy/wealth and energy consumption will increase across the board as developed countries get richer and developing ones catch up. This projection does not take into account the energy savings from the development of new, more energy efficient power generation or end use technologies. On the other hand, it doesn't account for the many new sources of energy demand such as the growing need to fuel such energy intensive operations such as water desalination to meet an almost insatiable demand for fresh water. The reality is that by the end of this century the world will in all likelihood be using energy at 10 times its current rate.

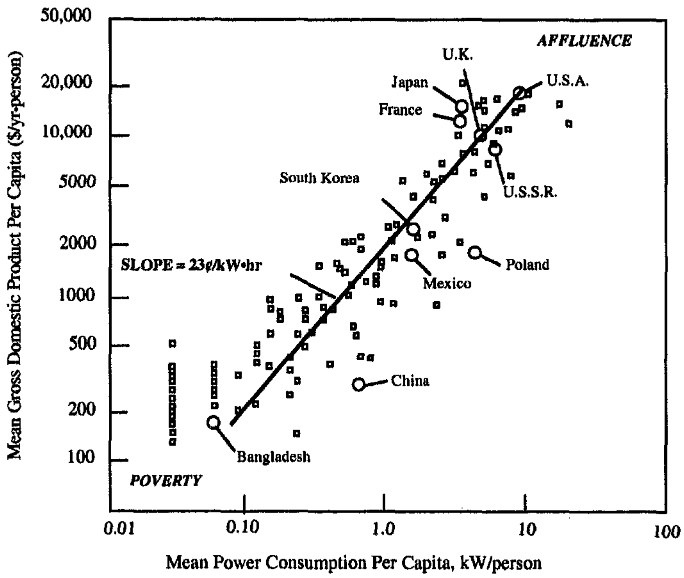

Figure 1. The relation between energy consumption and GDP, which is essentially equivalent to wealth[3]. Although plotted on a log-log scale, the relation is indeed linear as shown by the line which corresponds to 23¢ of GDP/kW-hr of raw energy consumption. Even though there is a scatter of about a factor of 2 for the individual points, the overall relation is valid over two orders of magnitude.

Existing world energy demand is currently being met through the use of fossil fuels, which supply about 85% of the world's energy. The dominance of fossil fuels is explained by their abundance, high energy density, convenience and ease of use, and most importantly their low cost. These attributes of fossil fuels have become requirements for all energy sources and are not likely to change. However an additional requirement is already on the horizon; the need for "clean energy." Power generation with minimal impact on the environment will imply technologies with zero airborne emissions. Fossil energy use today results in the yearly release of about 6 gigatons (Gt) of carbon to the atmosphere, or more than 20 Gt of carbon dioxide. In the US, the average per capita CO_2 emissions per year are approximately 20 tons. Aside from water and air, no other commodity is used at such a level. Together with the emission of CO_2, fossil fuels also result in large, but orders of magnitude smaller (but also orders of magnitude more harmful) releases of other pollutants into the atmosphere. These include SOx, NOx, fine particulates, mercury, and other trace elements. The levels of emissions are noticeable on both regional and global scales: smog is widespread in metropolitan areas; particulate emissions from power plants have known health impacts and decrease visibility hundreds of miles from their location. Global atmospheric CO_2 levels have already increased by 30% over their pre-industrial values and are now greater than at any time in the last several million years. In spite of these negative impacts, the use of energy, in bringing about the modern standard of living, has resulted in greatly increased life expectancy and vast improvements in the quality of life. Paradoxically, this abundance of energy wealth allows us the 'luxury' of worrying about and developing ways to mitigate the damage to the environment and also to generate the wealth needed to address these difficult environmental issues.

When considering the scale of current emissions, and the order of magnitude growth possible and actually desirable from the point of view of enhancing the quality of life for the world's population, it becomes clear that, unless corrective action is taken, there will be large impacts on the global environment. It is furthermore evident that likely improvements in reducing emission rates will not even be able to keep up with the increase caused by the development that will hopefully raise the standard of living for the world's population as a whole.

Based on this evaluation we have undertaken the task of developing truly zero emission technologies, while looking at options to permanently sequester the CO_2 generated by all fossil fuel consumption on a scale comparable to the fossil fuel supplies. To date, our emphasis has been on the most conventional fossil fuel available, coal, of which there are sufficient supplies to meet the world's energy demands for centuries to come, even at greatly accelerated rates of use. The foreseen need to permanently sequester all the CO_2 produced, coupled with the realization that coal is 'dirt' cheap, and that in terms of mass, about 3.7 times as much CO_2 leaves a power plant as carbon in the form of fuel enters the plant, implies that simply handling the CO_2 is likely to be comparable to the cost of the fuel. As such, fuel associated costs for new power plants are likely to effectively double. Fortunately, for coal plants these costs are a small fraction of the total cost. Given the great expansion of volume in turning solid carbon into gaseous carbon dioxide that must now be fully contained at the plant, transported, and then permanently sequestered, there will be a significant premium on attempting to increase the power plant efficiency. This emphasis on efficiency results from the realization that for the same amount of product energy, much less fuel will need to be consumed and much less waste handled. Even allowing for the compression of CO_2 into a liquid, (which is less dense than coal or water), there will still be several times more volume of CO_2 than coal. The compression of the CO_2 to a liquid state also involves an energy penalty. With the massive changes these considerations imply, it is evident that new power plants will have to be redesigned from scratch and that emphasis must shift toward maximizing efficiency. Cost analyses have also concluded that attempted retrofits to existing power plants will not be cost effective[4]. Furthermore, in order to avoid the never-ending series of upgrades as environmental rules continue to become more restrictive, one's goal should be to eliminate all airborne emission by design.

The ZEC Technology

The Zero Emission Carbon technology proposed by Los Alamos National Laboratory is a highly integrated electric power production concept that is estimated[5] by Nexant, Inc. to be capable of converting approximately 70% of the fuel energy (HHV) into electricity while releasing no emissions to the atmosphere and while producing a pure stream of liquid CO_2 at 1000 psi that is ready for sequestration. The concept is schematically illustrated in figure 2. The dry coal or other carbon source is gasified with a hydrogen-rich stream to generate a methane rich gas stream in an exothermic hydrogasification reaction. The energy release is used to make up for any energy losses and also generate limited amounts of water gas. The methane rich product stream is run through a high temperature particulate filter and scrubbed of most of its sulfur using a small sacrificial bed of CaO or $CaCO_3$. The resulting gas is passed at temperature to a carbonation vessel in which the methane is reformed and shifted with steam in the presence of CaO to produce a hydrogen rich stream. The CaO reacts with the CO_2 byproduct to form $CaCO_3$, thereby removing one of the product gases and keeping the reaction moving forward. At the same time, the production of $CaCO_3$ is an exothermic reaction, which releases a sufficient amount of heat at the required temperatures to drive the methane steam reforming reaction. The resulting product stream of hydrogen is split; the half effectively resulting from the hydrogen bound up in the input methane being recycled to gasify the next batch of coal. The other half (effectively resulting from the hydrogen originally bound up in the input steam) is sent to a solid

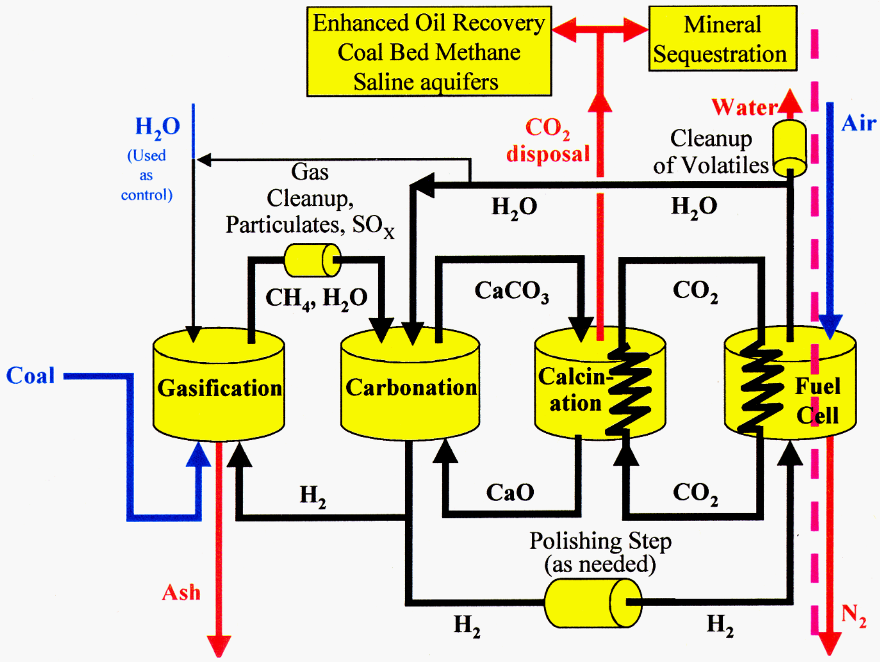

Figure 2: A schematic of the ZEC process. Material flows are idealized to the predominant components. The major reactions are as follows:

Gasification Vessel:	$C + 2H_2 \rightarrow CH_4$,	and some	$C + 2H_2O \rightarrow CO + H_2 + H_2O \rightarrow CO_2 + 2H_2$
Carbonation Vessel:	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	and	$CaO + CO_2 \rightarrow CaCO_3$
Calcination Vessel:	$CaCO_3 \rightarrow CaO + CO_2$	**Fuel Cell:**	$2H_2 + O_2 \rightarrow 2H_2O$

oxide fuel cell (SOFC) to produce the electric output of the plant. The inevitable waste heat produced by the SOFC is transferred to a calciner, which breaks the $CaCO_3$ that was produced in the carbonation vessel back into CaO that is recycled, and a pure stream of CO_2 that is sent to the sequestration plant. The CaO now carries the waste heat energy from the fuel cell in the form of usable chemical energy that is used to drive the hydrogen production occurring in the carbonation unit. The heat carried by the CO_2 gas leaving the calciner is extracted and used to drive a steam generator that generates the power needed to compress the now cooled CO_2 to 1,000 psi liquid CO_2. The steam produced in the SOFC during the oxidation of the hydrogen fuel is recycled back to the carbonation vessel where it is reacted with the next batch of methane produced from the next batch of coal. Removal of contaminants originating from the coal and present in the internal gas streams of the process are removed via a slipstream. This will be discussed in more detail in a later section. The ZEC process relies heavily on recycling of both energy and product streams to achieve its high efficiency while at the same time achieving zero emissions. In light of the recycling, there is no attempt to achieve 100% single pass reaction completion in the ZEC concept. The process also attempts to avoid large swings in temperature wherever possible and will employ heat recovery where this is not possible. More details on the ZEC concept can be found in the earlier process evaluation by Nexant, Inc[5]. We also point out that these concepts of recycling are likely to be key elements in any future power plant and that the ZEC process can be adopted to produce a hydrogen product stream for external use. We now turn the discussion to our work in forwarding the various recycling elements.

Hydrogasification

ZECA Corporation contracted with the Gas Technology Institute[6] (GTI) to examine the hydrogasification properties of several different coals including a subbituminous coal from the Antelope Mine in the Powder River basin and Saskatchewan lignite on which initial gasification tests have been

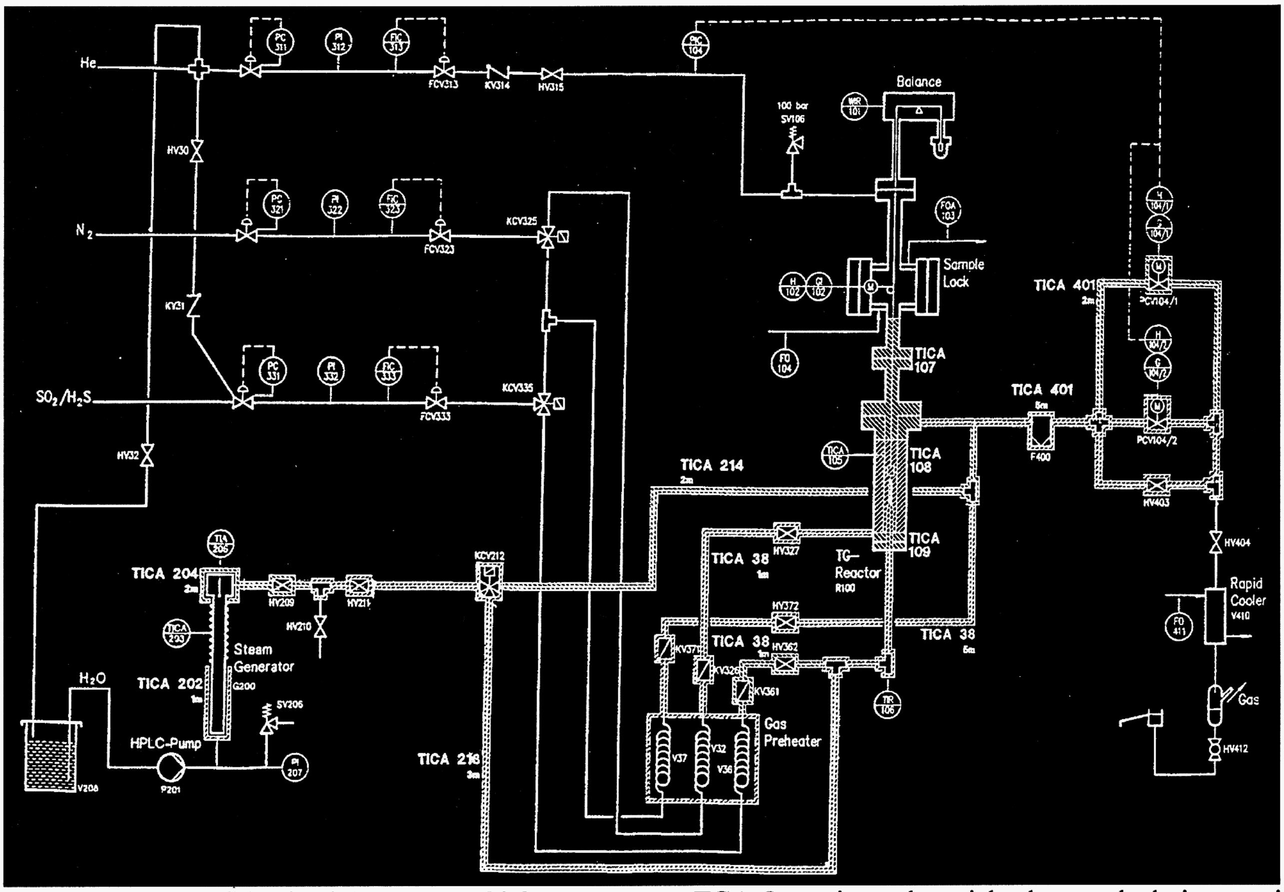

Figure 3: Schematic of GTI's high pressure, high temperature TGA. It continuously weighs the sample during reaction, with an accuracy of 10 μg.

completed. Several additional samples await testing. In addition to the this work, the Illinois Clean Coal Institute[7] has funded a set of hydrogasification tests on an Illinois #6 bituminous coal that has higher sulfur levels. The initial work looked at the fractional gasification achieved using pure hydrogen, or 50/50 volume mixtures of steam and hydrogen. All tests were carried out at various pressures up to 1,000 psi and several different temperatures around 900°C. The choice of these conditions involves a tradeoff between the reaction kinetics, which favor higher temperatures and higher operating pressures for the hydrogasification reaction, and the maximum temperature set by the subsequent carbonation reaction; the $CaCO_3$ breaks down at temperatures above 900°C at partial CO_2 pressures of 1 atmosphere.

The tests used the apparatus shown in Figure 3. The apparatus is a high-temperature, high-pressure thermogravimetric analyzer (HPTGA) which records the mass loss of the coal sample with time. Pre-reaction and post-reaction measurements of the samples tested were used to confirm the HPTGA results. The procedure used entails the following sequential operations: sample preparation; purging of the HPTGA with an inert gas; heating of the reaction zone to the desired temperature; starting of the reactive gas flow; dropping the sample into the reaction zone; continuous recording of the weight change; and recording the product sample final weight. The time dependence of the fractional conversion of the carbon contained in the coal to a volatile phase are shown in figures 4, 5, and 6, for a variety of different conditions and for the bituminous, subbituminous, and lignite coals respectively. The details of the results from the analysis of the Illinois coal, char, and the hydrogasification are given in Table 1. The runs were terminated when the mass of the system no longer changed. The final masses of the product material were obtained and used to confirm the fractional conversions as determined by the mass changes seen during the runs.

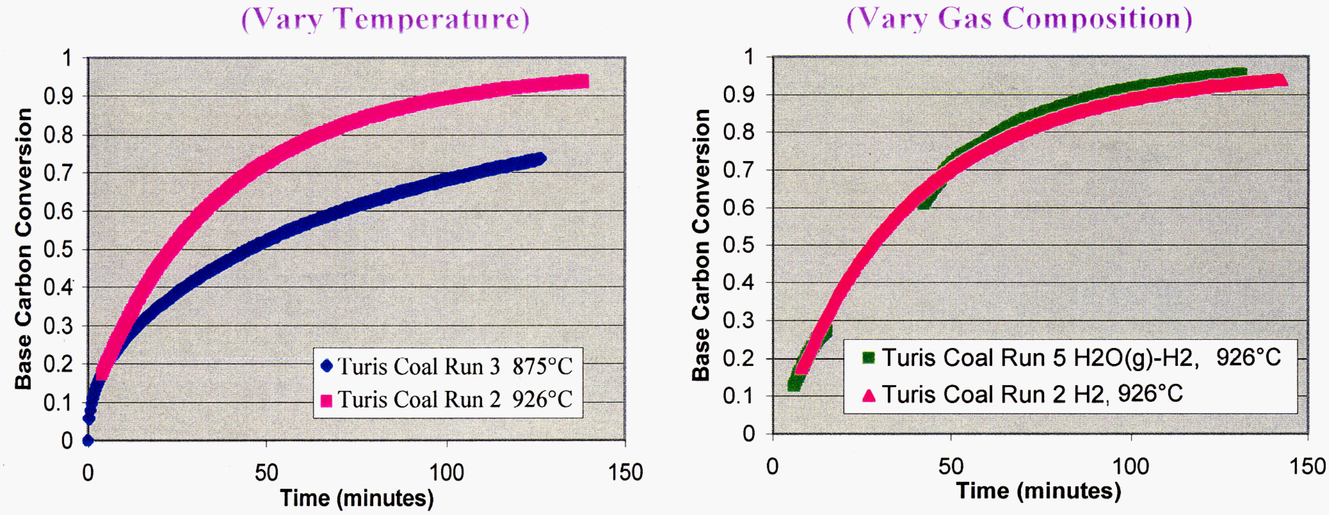

Figure 4: Conversion results for the Illinois bituminous coal. The results show the fraction of the carbon converted to volatile compounds based on the mass changes of the samples as determined by the HPGTA. The left graph shows the fractional conversion using hydrogen at a pressure of 996 psi at temperatures of 875°C and 926°C. The right graph shows the fractional conversion obtained at a temperature of 926°C and a total system pressure of 996 and 1015 psi, for a pure hydrogen atmosphere and for a 50/50 molar ratio of steam and hydrogen respectively.

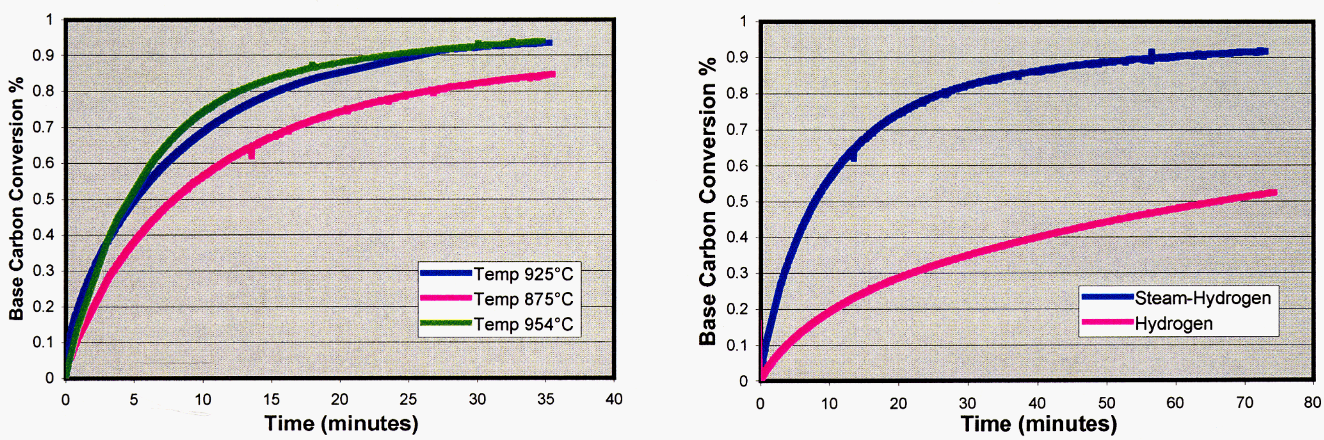

Figure 5: Conversion results for the Antelope subbituminous coal. Left: Base Carbon Conversion vs. Time, Antelope Coal Char, Steam-Hydrogen; Right: Base Carbon Conversion vs. Time, Antelope Coal Char, Temperature 875°C

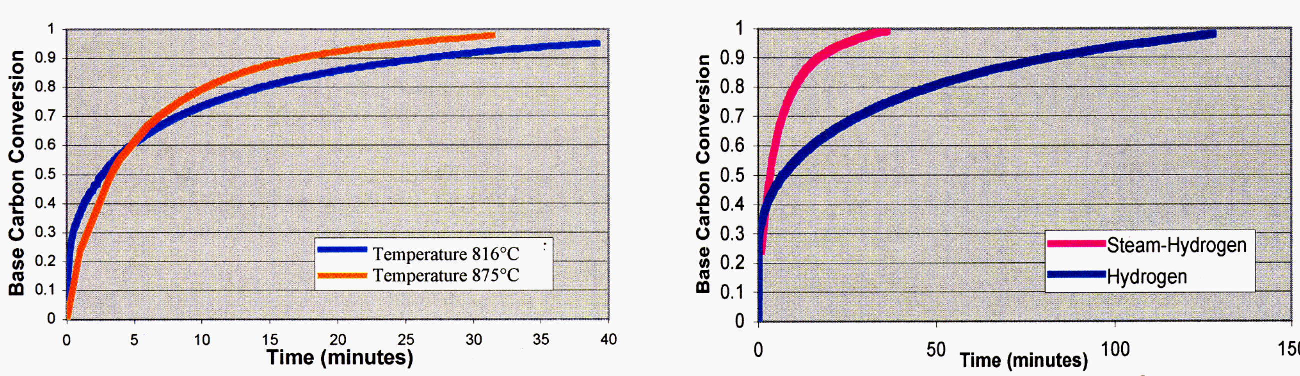

Figure 6: Base carbon conversion vs. time for Saskatchewan lignite. The left picture compares the results at 2 temperatures for a 50/50 mixture of H_2/H_2O at 798 psia, while the right picture compares the use of pure H_2 vs. a 50/50 mixture of H_2/H_2O at 875°C and 798 psia.

Table 1: Analysis results of the Illinois coal, resulting char, and hydrogasification of the char.

Illinois #6 Turis Coal Analysis (Starting Coal)			
Proximate Analysis, wt%	**(As received)**	**Ultimate Analysis, wt%**	**(Dry basis)**
Moisture	17.02	Ash	10.95
Volatile Matter	31.85	Carbon	70.14
Ash	9.09	Hydrogen	4.93
Fixed Carbon	42.04	Nitrogen	1.49
		Sulfur	4.13
		Oxygen, by diff	8.36
Illinois #6 Turis Coal Char (after charring at 871 °C)			
Proximate Analysis, wt%	**(As received)**	**Ultimate Analysis, wt%**	**(Dry basis)**
Moisture	0.89	Ash	14.49
Volatile Matter	18.50	Carbon	72.53
Ash	14.36	Hydrogen	3.06
Fixed Carbon	66.25	Nitrogen	1.55
		Sulfur	3.59
		Oxygen, by diff	4.78
Illinois #6 Turis Coal Char (after charring at 1010°C)			
Proximate Analysis, wt%	**(As received)**	**Ultimate Analysis, wt%**	**(Dry basis)**
Moisture	0.89	Ash	18.03
Volatile Matter	6.80	Carbon	75.40
Ash	17.87	Hydrogen	1.33
Fixed Carbon	74.44	Nitrogen	1.47
		Sulfur	3.14
		Oxygen, by diff	0.63

Fractional Carbon Conversion for Illinois Coal Runs				
Gas	**H_2 (Run 2)**	**H_2 (repeat of Run 2)**	**H_2 (Run 3)**	**$H_2O(g) - H_2$ (Run 5)**
Temp °C	926	926	875	928
Pressure psig	996	996	996	1015
Carbon Conversion %	97.2	96.4	87.4	97.1

It should be noted that in the case of the Illinois coal, the coal was charred in an inert atmosphere prior to hydrogasification run. The results shown in figure 4 and given in Table 1 were corrected to reflect this and give values relative to the starting coal, not the charred coal. The charring was dictated by sample agglomeration and the evolution of high molecular weight volatiles from the coal, which are known to adversely effect the performance of the HPTGA.

In the case of Antelope Mine subbituminous coal runs, the samples for all the runs were also charred in an inert atmosphere and the results were corrected to reflect this. Here, the charring was necessitated by the exteremly rapid mass loss that occurred even as the sample was being lowered into its final location in the HPTGA. The lignite samples were not charred and hence no corrections to the data were required.

We find the results obtained highly encouraging both in terms of the temperature (compatible with the ~900°C limit set by the CaO carbonation reaction) and the high overall carbon conversion fraction.

Coal Compatible Fuel Cells

Fuel cells play a critical part in the ZEC process and are likely to be integral parts in any other advanced coal process. In the ZEC process, the SOFCs produce the electric output through the electrochemical reaction of hydrogen with a pure oxygen stream; the SOFC's providing the pure oxygen stream as they also act as an integral oxygen separation membrane. The fuel cells also produce a large amount of high temperature, high quality waste heat which is harvested and transferred back into the ZEC process in a very useful form. Aside from temperature drops needed to move the heat energy, the heat energy is all available at essentially the fuel cell temperature. This is one of the key advantages provided by SOFC's in addition to their relatively high intrinsic conversion efficiency from fuel energy to electrical energy, typically about 50%. The fuel cells required for the ZEC process are however not the same as the SOFC's currently beginning to enter service for the natural gas market. In fact, they have a number of unique requirements that sets them apart from the current SOFCs. As such, we call these new fuel cells Coal Compatible Fuel Cells, or simply CCFCs. The requirements for the CCFCs† that go beyond those of the current natural gas SOFCs are:

1) The ability to perform with an inherently 'dirty' fuel such as coal; foremost of which is the need for sulfur tolerance, preferably at the 100 ppm to 1000 ppm level.
2) Higher as opposed to lower operating temperatures. In order to facilitate the heat transfer, which needs to operate the calciner at about 900°C, an operating temperature of 1100°C or higher would be desired.
3) An integral heat transfer system must be incorporated into the fuel cell to remove the roughly 50% of the input hydrogen fuel energy that is converted to "waste heat" in the process of the electrical power generation.
4) The ability to maintain complete separation between the fuel/fuel exhaust side of the fuel cell from the air side.
5) The ability to operate at the higher pressures that are typical of coal gasification facilities.

At LANL we have begun the search for a sulfur tolerant anode material for the CCFC's. The poisoning effect of sulfur in the fuel (in our case predominantly in the form of H_2S) on the standard Ni/YSZ anode of SOFCs has been studied in detail[8,9,10]. It has been reported that even parts per million (ppm) levels of H_2S can cause significant (up to 15.6% drop in voltage at 1000°C for 10 ppm of H_2S) performance loss at the anode[8]. This performance loss is completely recoverable at low (<15 ppm) concentrations of H_2S[9] and is only partially recoverable at H_2S concentrations >100 ppm[10]. Although the exact mechanism of this poisoning is not well understood, these results indicate a need for effective sulfur removal before the fuel is fed into the conventional SOFCs. The development of electrodes that are tolerant to H_2S would greatly decrease the cost of the sulfur cleanup and open the possibility to directly operate SOFC's on a coal derived fuel.

The development of new anode materials will depend on a basic understanding of the poisoning mechanism and the development of materials and/or designs to increase the tolerance to sulfur. To elucidate the poisoning mechanism, various anode components were subjected to a severe H_2S treatment. Samples of Nickel (Ni), 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ), 20 mol% Gd_2O_3 doped CeO_2 (GSC), and Copper (Cu) were all placed in a 1000 ppm H_2S/90%H_2/4%H_2O/Balance N_2 atmosphere. These samples (both powder and polished pellets) were heated at 10°C/min to 1000°C for 8 hours and then furnace cooled to room temperature. The phases present in the samples were then analyzed using

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† Without an active program to develop CCFCs, the future of the coal industry is in doubt. Today's fuel cell development efforts all concentrate on clean natural gas or hydrogen fuels and the resulting fuel cells are fundamentally incompatible with the inherently "dirty" fuel gases derived from coal and the other "coal" needs discussed above. Once the natural gas fuel cells capture a large share of the energy market, they will continue to squeeze coal out of the picture.

X-ray diffraction and the composition of the samples was analyzed using X-ray Fluorescence (XRF). X-ray diffraction revealed that the GSC sample had decomposed to a cerium oxy-sulphide phase (Ce_2O_2S), while the remaining samples (YSZ, Ni and Cu) were all single phases. However, when the polished pellets of these samples were examined using XRF there was a clear sulfur peak present on all the samples except YSZ. This shows that the surface of the Ni or Cu catalyst is being deactivated by the H_2S either due to adsorption or surface reaction while the YSZ is clean. Hence any new anode development should concentrate on the replacement of the Ni in the anode with an electronic conducting material that will not be affected by the H_2S.

There are various perovskite oxides that possess the necessary conductivity and thermodynamic stability to operate in SOFC anode conditions. These include the $La_{1-x}A_xBO_{3-x}$ and $LaB_{1-x}A_xO_{3-x}$ oxides where (A = Sr, Ca or Mg and B = Cr or V). Thermodynamic calculations on the Cr-based oxides revealed that these are more resistant to poisoning from H_2S than the Ni or Cu metals[11]. When these chromate-based perovskites were subjected to the same severe H_2S treatment as the Cu and Ni metals, there was no sulfur present on their surface. Hence, these perovskites when mixed with the YSZ should be potential sulfur tolerant anodes.

A $La_{0.8}Sr_{0.2}CrO_{3-x}$ (LSCO) composition was selected for the SOFC anode testing. This perovskite powder with a specific surface area of 3.98 m^2/gm was mixed with an equal weight of YSZ with a specific surface area of 10.49 m^2/gm and then ball milled for 6 hours. The resulting powder was mixed with ethylene glycol and brush painted on a 1/2" diameter YSZ disc (0.5 mm thick). Platinum current collectors and counter and reference electrodes were then painted on to the YSZ disc to form the single-SOFC (Figure 7). A NiO(60wt%)/YSZ(40wt%) electrode was prepared in an identical manner to serve as the baseline for comparison. The single cells were then sealed onto an alumina tube using a glass (EG 2705) seal and heated to 1000°C where they were tested. The cathode and reference electrodes were exposed to an air atmosphere while the anode was exposed to H_2/H_2O mixtures with varying concentrations of H_2S.

The performance of the Ni/YSZ and LSCO/YSZ anodes at 1000°C in the presence of 0 and 1000 ppm of H_2S is shown in Figure 8. Both the Ni and LSCO based anodes had comparable performance in a $90\%H_2/4\%H_2O$/balance Argon fuel (Anode specific resistance of approx. 4 Ωcm^2). However, when 1000ppm H_2S was introduced into the fuel stream the performance of the Ni-based anode degraded by >60% while the performance of the LSCO based anode was unaffected. Figure 9 shows the poisoning effect of 10 ppm and 1000 ppm H_2S on the Ni and LSCO based electrodes. Although the H_2S was kept on for only a few hours (overnight runs were not allowed due to safety considerations), during these experiments, the results indicate that the LSCO based anodes are much more resistant to sulfur poisoning than the conventional Ni-based anodes.

It should be noted that the morphology and composition of these electrodes are not optimized. The LSCO/YSZ anodes need to be optimized and their polarization needs to be decreased by almost an order of magnitude. Moreover, longer-term exposure of these anodes to H_2S needs to be studied before these anodes can become commercially viable.

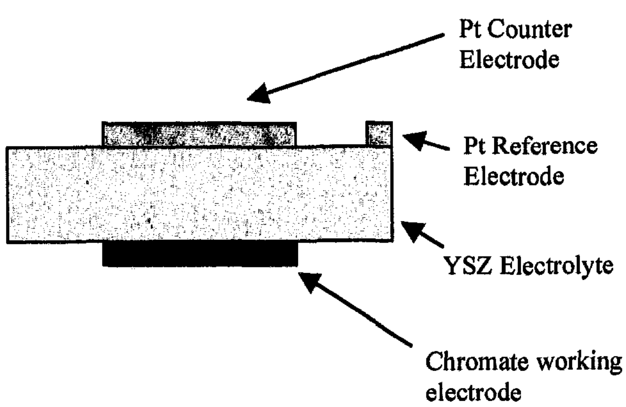

Figure 7: Schematic of Experimental Setup

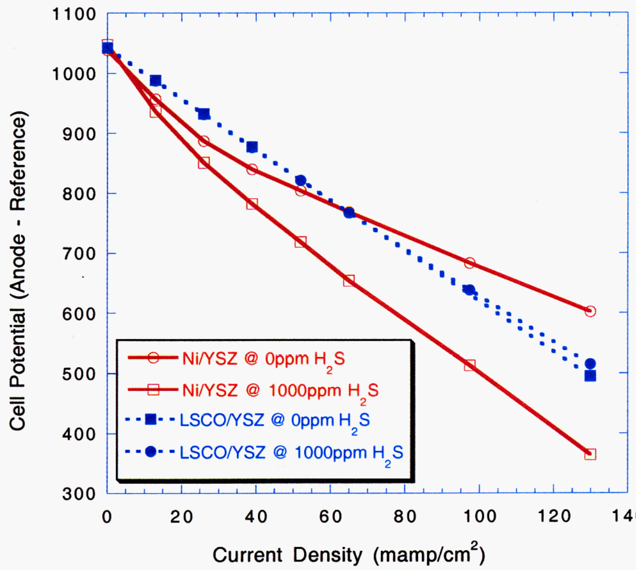

Figure 8: Performance of the Ni/YSZ and LSCO/YSZ anodes in the presence of H_2S at 1000°C.

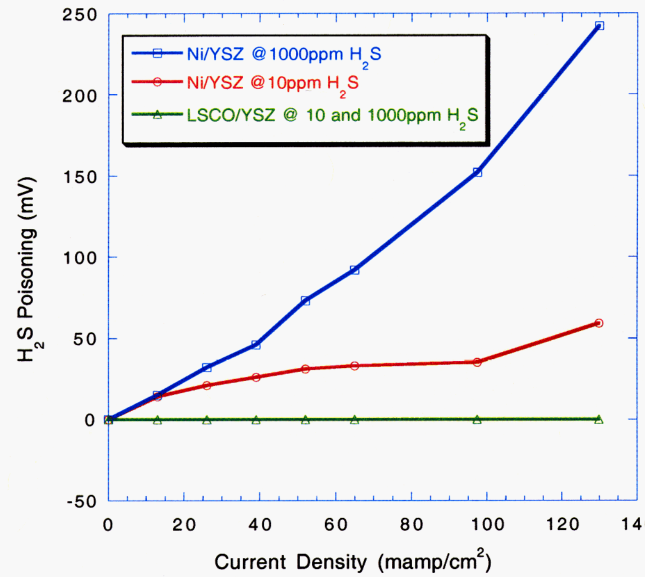

Figure 9: H_2S poisoning of the Ni/YSZ and LSCO/YSZ anodes in 10 and 1000ppm H_2S at 1000°C.

After further work to improve the gas permeability of the new sulfur tolerant anodes, we will move to testing the performance at temperatures above the 1000°C limit imposed by the glass seals used in the current test configuration. Evaluation of the requirements for the associated heat transfer system is also beginning. This work will also be applicable to the calciner and likely any advanced coal process regardless of the gasification route pursued. The various major coal gasification reactions including those of ZEC, direct water-gas production from coal, and the production of CO from coal through the Boudouard reaction, all require nearly identical amounts of heat transfer in order to proceed and all operate in a similar temperature regime. Finally, higher operating pressures for the fuel cells is currently foreseen as being accomplished through operating the fuel cells inside a pressure vessel in which there is at most a small pressure difference between the pressure within the fuel cells and the pressure vessel.

The Calcium Oxide/Calcium Carbonate System

The concept of using calcium oxide and its carbonation to aid in coal gasification dates back to at least the early 1900's[12]. The reverse reaction, calcination of lime, which is also required by the ZEC process, is a commercial process used in the cement and other industries. Fixed bed or rotary kilns and fluidized bed equipment are used to calcine limestone by directly contacting the limestone with hot flue gas. In the direct heating process, the carbon dioxide from the limestone becomes mixed with the flue gas, causing significant greenhouse gas emissions. The ZEC technology differs from the industrial processes because the ZEC calcination process produces a pure CO_2 stream and involves no combustion process to produce the needed heat. Instead, the heat from the SOFC is supplied to the calcium carbonate to release the CO_2. Calcination and carbonation tests related to CaO assisted hydrogen production from methane have been performed at the laboratory scale[13]. Previous work concerning the use of the $CaO/CaCO_3$ to drive coal gasification includes the work associated with the CO_2 acceptor process[14].

In addition to the overall ZEC process study performed by Nexant, Inc., ZECA funded a study by NRCan/CETC[15] to examine the $CaO/CaCO_3$ part of the ZEC system in more detail.

The conclusions of this study were that:

The potential problems associated with the design of the ZECA reactor have been examined. It is our considered opinion that based on this study the ZECA reactor concept appears to be feasible. However, there are a number of important issues that must be addressed. In particular, the reactor may function in a severely limited way as a gas cleaning step for removal or destruction of nitrogen species, and some heavy metals.

There are also two choices of operation: either via melts...), or with solids. The view expressed here is that for a practical process melts should probably be avoided. (In the body of the report, it is indicated that this should not be a problem *"if the reformer/carbonator is operated at conditions under which the $Ca(OH)_2$ melt is not formed, melting should not occur at temperatures below 1010°C."*) *Crucial issues will be limestone behavior, especially sintering, attrition and agglomeration, and detailed characterizations of limestones under the final conditions chosen for the reactor will be critical in order to make a good selection.*

The most important issue for continuous operation of the reforming and carbonation process is circulation of the CO_2 sorbent through a retained bed of catalyst. A pressurized circulating fluidized bed would meet the requirement. The catalyst particles can be maintained in the reactor by grids, which allow the sorbent particles to pass through, whereas the sorbent is circulated between the reactor and the calciner. An inherent tendency of segregation for particles with different density and size would effect the separation of the catalyst and the sorbent in the bed.

There is another critical issue regarding the pressure level for the reformer/carbonator. In a patent concerning a reforming process with a carbon dioxide acceptor it was stated that lime sorbent should not be used at steam partial pressure higher than 13 atm, above which individual lime and calcium carbonate particles tend to agglomerate and a gas-impermeable mass would form rapidly. It was also stated the critical level of steam partial pressure for other lime bearing minerals such as dolomite is substantially the same, and that inert diluents would offer no solution to this problem.

In the ZECA design, the pressure for the first reformer is 60 atm, and the partial pressure of the steam will be well above 13 atm. In the event that serious agglomeration occurs, not only would a fluidized bed cease to function, but a fixed bed might also be blocked. Lowering the steam pressure by reducing the steam to carbon ratio would lower the conversion, and might result in carbon formation, which leads to deactivation and overheating of the catalyst. Accordingly, agglomeration should be carefully checked in any preliminary screening work.

For the proposed pressurized fluidized bed, we believe it is possible that, with highly agitated fluidizing of the particles, the steam partial pressure could be reduced through more rapid reaction with CH_4 and CO and quicker mixing with the product gas. The steam may be introduced from a series of entrances along the bed height, to keep its partial pressure below the critical level by mixing it with the reacted gas. However, the issue of whether the agglomeration problem can be overcome by this configuration should be carefully investigated. If the agglomeration cannot be avoided, the operating pressure of the first reformer/carbonator would have to be lowered.

We note that the calcium oxide/calcium carbonate system is not viewed as a major player in the gas system cleanup, with the possible exception of halogens and sulfur. Even in these cases, the removal efficiency need not be very high in a single pass of gas through the system. This is discussed in more detail in the following section. The agglomeration issue and the possible need to reduce the overall pressure in the reforming step needs to be investigated in more detail. We however also note that these issues were successfully addressed in the 1970's CO_2 gas acceptor process pilot plant[16, 17].

Coal Contaminant Removal and Recycling

In the preceding section we have discussed the removal of CO_2 through the use of calcium oxide. In addition to removing this major product of the coal gasification process, the exhaust stream leaving the fuel cells must also be cleaned, as will the various other gas streams internal to the ZEC process. Clearly, any contaminants that are introduced with the coal will have to be extracted and eventually turned into a useful product or disposed of in a safe, inert form. Although not trivial, we assume that separation of the solid phase ash components, including particulates, can be handled directly as part of the gasification step and will not be discussed here other than noting that by maintaining a system with a fully contained gas flow they won't be released to the atmosphere and that work is ongoing in this area, as it is a common issue for all coal gasification processes.

Sulfur will be addressed to the roughly 1000 ppm level which we believe the CCFC's will be ultimately tolerant of. Calcium oxide and calcium carbonate are sorbents capable of removing sulfur to such levels and doing so at the temperatures resulting from the gasification step. Here again, we will initially rely on the ongoing work in this area to meet our needs. There are also some advanced sorbents which may remove sulfur to even lower levels at the desired temperatures, and failing that, one can always adopt the undesirable option of cooling the gasification product stream to the temperatures that the more conventional sulfur removal agents work. A relatively new product for hot gas cleaning is the sorbent RVS-1 being offered by Sud Chemie. RVS-1 can be used in fixed bed environments with temperatures to 760°C at 20 atmospheres. Tests with RVS-1 show removal of sulfur compounds down to the 15 to 30 ppm level. Informal discussion with Sud Chemie indicates that in certain conditions the sorbent can clean the gas to 10 ppm of sulfur. RVS-1 was developed as part of a US DOE program and information can be found at the url: http://www.netl.doe.gov/newsroom/tipsheets/netl%5Frocks.html

In a recent study, Kiningen and Sjostrom[18] reported reforming methane with a sulfur-deactivated Haldor Topsoe catalyst HTSR1. The sulfur contents of the feed gas varied from 25 to 300 ppm. At 800°C and above, no catalyst deactivation was observed in HTSR1 for hydrogen sulfide levels up to 200 ppm. This is important to the ZEC reforming/carbonation step, which operates in the temperature regime of 800°C. The potential to clean the ZEC raw synthesis with the Sud Chemie sorbent RVS1 so that the HTSR1 catalyst can be used for reforming needs to be investigated in more detail with the respective manufacturers.

The lower temperature sulfur removal options include zinc ferrite and zinc titanate as two sorbents that were developed to the pilot plant scale and extensively evaluated. The sorbents are capable of reducing the hydrogen sulfide concentration in synthesis gas to less than 20 ppm in a fluidized bed reactor. Zinc ferrite can be used up to about 550°C; above this temperature it loses structural strength and begins to vaporize. The zinc titanate sorbents (prepared by a proprietary granulation technique) show excellent sulfur capacity, regenerability and the required resistance to zinc vaporization up to about 650°C.

As the ZEC process involves no combustion of the coal, NOx generation is of no direct concern, especially in the reducing conditions that exist in the entire process with the exception of in the CCFCs. However, the nitrogen that typically amounts to about 1% of the mass of the coal, will have to be extracted to prevent internal buildup. Nitrogen species likely to be released at the ZECA gasifier temperatures will be predominantly nitrogen gas and perhaps some NOx. Failure to reach equilibrium condition may also result in the presence of some other nitrogen containing compounds. At lower temperatures one will begin to favor NH_3, NO_x, N_2O and HCN arising from the fuel nitrogen content of the coal. Further, it is known that calcined limestone is an active catalyst for the following two reactions[19]:

$$NO + CO = 1/2N_2 + CO_2 \qquad \text{and} \qquad NO + H_2 = 1/2N_2 + H_2O$$

The reasonable expectation is that the reformer/carbonator will allow for the conversion of NO to N_2. In the case of HCN and in the absence of O_2, CaO is capable of acting as an agent to capture HCN via two overall reactions:

$$2HCN + CaO = CaCN_2 + H_2 + CO \qquad \text{and} \qquad 4HCN + 2CaO = 2CaCN_2 + C(s) + CO_2 + 2H_2$$

Possible products reported in the range of 200-700°C include $Ca(CN)_2$, $Ca(NCO)_2$ and $Ca(OH)_2$, but above 700°C, the primary product is known to be $Ca(CN)_2$. Hence, it is reasonable to postulate that for minor amounts (i.e., ppm) of NO and HCN expected from a vigorous hydrogasification step, the reformer/carbonator may well act to "capture" or destroy these species.

From the large concentrations of hydrogen present as the result of the hydrogasification itself, one would expect that the main nitrogen species would ultimately be NH_3, certainly at least in the low temperature realm. At the higher temperatures present throughout most of the ZEC process ammonia is thermodynamically unstable, but may still exist as the species is meta-stable from a kinetics perspective. Based on these observations nitrogen will probably be recovered in the form of ammonia as the result of processing part of the gas stream at lower temperatures to produce the NH_3, which will then be scavenged from the system.

Removal of trace elements such as mercury will probably be accomplished by scavenging them from the system at lower temperatures through the use of chemical sorbents. At LANL, we have recently begun an investigation of the removal of mercury in the reducing conditions present in the ZEC process and hope to have some results available in the near future.

In the preceding sections we have discussed the chemical reactions that could be used to remove CO_2 and the other contaminants introduced by the coal, but not the process by which this would be carried out. We note that in the ZEC process there is an extensive reliance on recycling of both energy and the oxidation step product gases back to the gasification step, and we plan to make use of this recycling to also handle the contaminants. We begin this discussion by looking at the removal of steam/water from the process.

The removal of the water is most easily accomplished by condensing it, but careful integration of this into the overall design is again a very important consideration, as condensation can result in large losses of efficiency. As noted earlier, the gasification of the coal requires a gas stream, be it steam, hydrogen, or CO_2. The gas stream required for the gasification process is very large, but always less than that produced in the oxidation step. As can be seen by examining the reaction equations given in Figure 2, for a pure carbon input and excluding the CO_2 produced from the coal that was input, the products from oxidation process need to be fully recycled for gasification purposes. However, when taking into account any water in the coal, or any hydrogen in the coal that is subsequently oxidized to form water, there will be excess steam available that will need to be removed from the recycle stream. For instance, even with all water removed, coal is approximately $CH_{0.8}$ instead of being pure carbon. When 1 mole of this coal is gasified, fully reformed, and shifted, two moles of steam are required and yield two "product" moles of hydrogen when reacted with the one mole carbon from the coal. In addition, the 0.8 moles of hydrogen in the coal represents another 0.4 moles of H_2 gas. The oxidation of the combined amounts of hydrogen yields 2.4 moles of steam, of which only 2.0 moles are needed for the next mole of coal. Thus 0.4 of the 2.4 moles or 16.67% of the steam generated during the oxidation step needs to be removed. Any water not removed from coal prior to its gasification will yield a larger fraction of the gas stream following the oxidation step that must be removed prior to recycling.

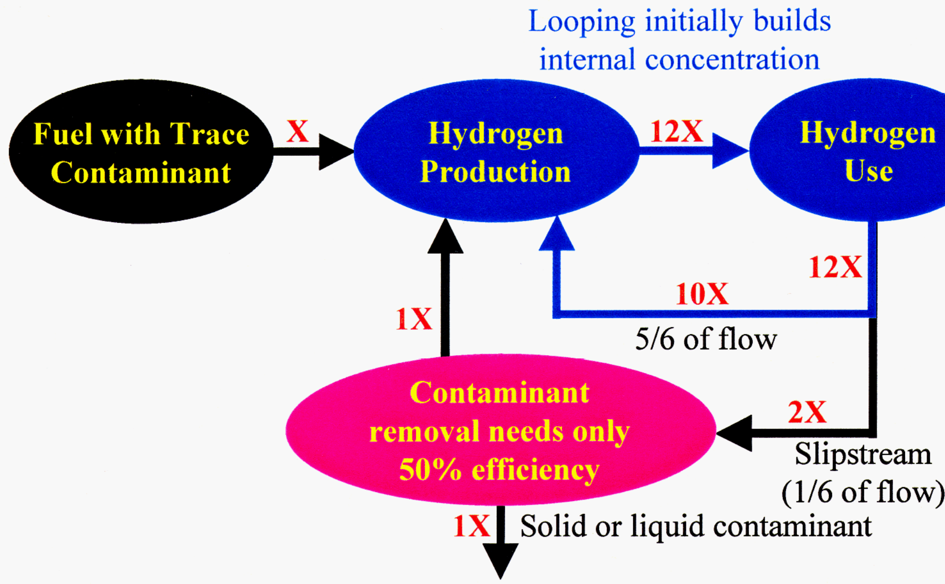

Figure 10: Concept for complete contaminant removal in spite of poor single pass efficiency. During a single fuel injection cycle an amount of contaminant X is injected. If 11 such injections take place before invoking the slipstream, internal contaminant levels grow to 11 X. On the 12th injection, following the hydrogen production step and hydrogen use step, the internal contaminant level becomes 12 X. At this point the slipstream path is open and we find that a removal process that only captures 50% of the contaminant flowing into it removes100% of the contaminant injected during this fuel cycle. We also note that the process now runs at steady state, with internal levels neither rising nor shrinking with time.

The need to remove part of the gas following the oxidation step and prior to the recycling step opens an opportunity to remove the contaminants introduced with the coal. At the same time, the need to recycle a large fraction of the oxidized product stream also opens up the opportunity to recycle any fuel components that were not oxidized due to incomplete oxidation during the oxidation step. By removing the CO_2 in pure form, and then fully containing the remaining gas stream, in each fuel injection cycle, one need only remove the amount of contaminants introduced by a single injection. In particular, as there are no emissions of the oxidation product gases to the atmosphere, it is not important which particular fuel injection the contaminants came from, but simply that the amount removed is equal to the amount injected. The general clean-up concept is outlined in Figure 10. In this figure, in each fuel injection step, an amount of contaminant X is injected as part of the coal. This coal/methane is effectively gasified/reformed/shifted with recycled oxidized gas (steam) and run through the oxidation step. The resulting oxidized gas, which now contains an amount of contaminant X, is fully recycled to gasify the next batch of coal injected. Following the resulting gases around the recycle loop this second time, we find that since none of the contaminant was removed, there is now an amount of contaminant 2X in the oxidized gas stream. If we repeat this process for say 12 cycles we now have an amount 12X of the contaminant present in the oxidized gas stream. However, in this loop, we now enable a slipstream that accepts 16.67% or 1/6 of the oxidized gas stream and this gas is not directly recycled to the gasification step. The slipstream contains 1/6 of the gas flow and also 1/6 of 12X (or 2X) of contaminant. We note that the slipstream also contains the 16.67% of the steam, which in the example discussed in the preceding paragraph, needs to be removed in any case. This steam is condensed, thereby separating out the water and removing most of the gas volume of the slipstream. The remaining gas volume of the slipstream contains any unoxidized fuel components, any gas phase contaminants not condensed with the steam or absorbed into the resulting water. We now pass this much smaller gas stream, which we assume still contains the 2X of contaminant, over a chemical sorbent. In this case, we see that we need only remove 1/2 of contaminant contained in the remaining gas slipstream. Having removed 1/2 of the 2X of contaminant, we note that this is the same amount of contaminant injected during a single fuel cycle. The remaining 1X of contaminant, which was not picked up by the sorbent on this loop, is subsequently recycled together with the unoxidized fuel back into the gas flow somewhere prior to the oxidation step. In the next fuel cycle another unit of coal is injected, which contains an additional 1X of the contaminant. This coal is gasified by the 5/6 of the oxidation step product gases that did not pass through the slipstream during the previous fuel cycle. This recycled stream contains 5/6 of 12X of contaminant or 10X. Thus in this new fuel cycle we have 10X of contaminant from the non-slipstream recycled gas, 1X from the coal, and 1X of the contaminant that remains in the slipstream following the absorption step. This adds up to 12X again. We have now established a steady state solution in which an equivalent amount of contaminant is removed as is injected together with the coal in each cycle. This is done in spite of the fact that the absorption process only has an efficiency of 50%.

Such a process greatly eases the performance requirements on the sorbent. We no longer need sorbents that for instance may be required to remove 99.9999% of a harmful contaminant if the oxidation gases were released to the atmosphere. The requirement of condensing out the water from the slipstream also opens a broad temperature range in which other contaminants in the slipstream can be chemically absorbed. Through the use of recycling, we no longer need to be directly concerned with any unoxidized fuel gas. This gas is simply recycled through the oxidation step on the following fuel injection cycle. (Only a second order loss in efficiency is incurred, which is related to the energy penalty of pumping this recycled fuel through the system as second time and heating it back to the overall system temperature.) Along these lines, the price paid for removing 100% of the contaminant and avoiding any loss of unoxidized fuel is in the additional pumping costs and higher internal concentrations of the contaminants. However, one cannot allow the concentrations of the contaminants to reach a level at which they damage the internal components of the overall system. One must also assure that the additional pumping or heating requirements do not have a significant impact on efficiency.

Nevertheless, a number of open questions still remain. First, one will still need to properly dispose of the contaminants that came with the coal. The process described above only fully separates the contaminants; it does not dispose of them. Likewise, any contaminants that may be absorbed into the water produced from the slipstream will need to be removed from that water to meet environmental standards. The volume of water that must be dealt with is however much less than the volume of gases being released in current power plants, hopefully simplifying the task at hand.

Evaluation of Water Soluble Polymers on Mercury II Removal

The condensed water stream exiting the fuel cell will contain some of the more volatile elements such as mercury, arsenic and selenium, which will necessitate removal to acceptable discharge levels. For their removal we are evaluating water-soluble chelating polymers, which show selectivity for these targeted metals. Our initial focus has been on mercury, which in the condensed phase should exist as a soluble mercury II chloride salt. Thus far three polymers have been evaluated for mercury retention and removal a Low Molecular Weight polyehtylenimine (LMW PEI), a High Molecular Weight polyehtylenimine (HMWPEI) and a diol modified polyethylenimne (PEI Diol). Each polymer (0.1 wt%) was allowed to contact a pH adjusted aqueous solution of mercuric chloride (146 ppm) by shaking for 10 minutes. The solutions were filtered through a 10,000 MWCO ultrafilter and the permeate analyzed for mercury. The results of these two polymers for Hg retention at various pH values are shown in the Figure 11. Both the HMW PEI and the PEI Diol met the targeted level of <250 ppb Hg within the pH range of 4-6. For the LMW PEI Hg concentrations were slightly above that level within that pH range.

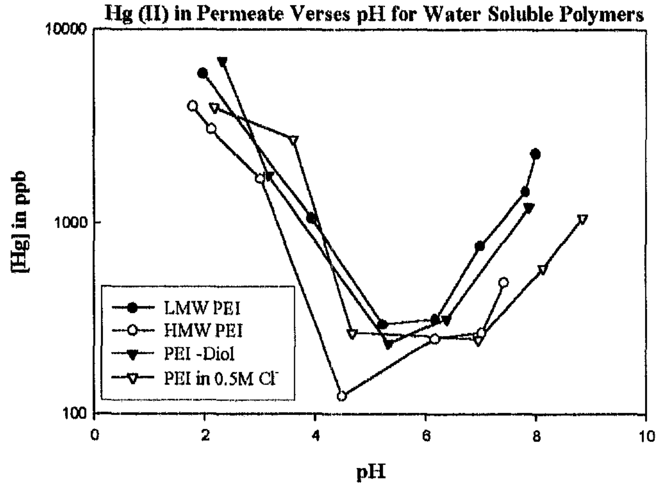

Figure 11: Mercury removal performance of water-soluble chelating polymers as a function of pH.

Indications are that this is a result of some polymer/Hg complex passing through the membrane because of its smaller size. In addition we ran the HMW PEI in the presence of 0.05 M chloride (PEI in 0.05 M Cl) to ascertain the effects of chloride salt of mercury retention. The result were similar to that obtained in the absence of chloride with some elevation of mercury concentrations.

Comments

Ultimately considerations related to the requirement of achieving zero emissions to the atmosphere from power plants will force their complete redesign. A large part of the redesign will involve a drive to high efficiency, necessary to reduce the costs associated with permanent CO_2 sequestration; the less CO_2, the lower the total sequestration costs. We also note that for today's power plants a significant fraction of the overall cost of the electricity produced and of the power plants themselves is in meeting current emission standards. With the upcoming tightening of particulate, SO_x, NO_x, and mercury emission standards in the US and elsewhere, the cost associated with emission reductions are expected to rise considerably. With an integrated system design that handles all emissions at once, substantial savings can be achieved, and it may be possible to achieve truly zero emissions (including those of CO_2) for the same price as simply meeting the upcoming round of emission standards. Making one's goal zero emissions from the outset sidesteps the issue of a never-ending series of retrofits to deal with ever tightening environmental regulations. At the same time it provides the opportunity to once and for all remove the image of coal as a "dirty" fuel, while at the same time forcing the rest of the fossil fuel industries to also fully address their emissions. The current path of slowly reducing emissions drives one away from coal and to natural gas, as that is the easiest path to a partial fix. Although the partial fix will in the long-term prove to be woefully inadequate, it would eliminate the coal industry

Conclusions

The ZEC process, whose development we have begun, has the goal of achieving zero emissions and reducing the costs associated with CO_2 sequestration by a factor of 2. This will be done by achieving twice the efficiency of today's power plants while also supplying a pure stream of high pressure CO_2 ready for sequestration, which will ultimately eliminate the emissions completely. Zero Emission Carbon is a key element in the achievement of the environmentally responsible use of fossil fuels and providing energy independence for this country.

To date no fundamental technical obstacles have been identified. We are very encouraged by the recent experimental results in which we have shown that sulfur tolerant anode materials are possible for SOFC, hydrogasification can achieve high conversion efficiencies in the needed temperature range, and that paths exist for the use of the $CaO/CaCO_3$ system and for contaminant removal from the overall process. In addition, the long history of work in the areas of hydrogasification, the CaO driven gas acceptor process, and the great strides made by the SOFC community provide a solid foundation for further progress. At the same time much work remains to be done on truly integrating the various aspects of the ZEC process or in developing other Zero Emission alternatives with similar characteristics. Based on the work done to date, it appears that solutions are being identified to ensure that the next true 'generation' of power plants can be available within 10 years or so and that they will be capable of providing the abundant, cheap and super clean energy that must be sourced from coal and other fossil fuels.

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